Chapter 1

GENERAL INTRODUCTION

1.1 Liquid state

A liquid is that state of matter which, when placed in a closed vessel, takes the shape of the vessel but does not necessarily fill the whole of its volume. The property that it takes the shape of the vessel distinguishes it from a solid and the property that it does not fill the whole of its volume distinguishes it from a gas. Unlike a solid, a liquid does not permanently resist forces tending to change its shape [1].

Studies of liquids were started from the very beginning of science itself. Their properties are very important in almost all branches of science. At a time, when the knowledge of molecular structure of matter was vague, liquid had been considered as a continuous medium and had developed its mechanics. This led to the creation of an old branch in physics called 'hydrodynamics'. Though this branch is a classical one, formulated by Newton, Bernoulli, Euler and Lagrange, much of its theories remain perfectly valid today inspite of the fact that
matter has a discontinuous molecular structure. With the advancement of the knowledge of the molecular nature of matter, it is natural to think about the relationships between the properties of individual molecules and the bulk or equilibrium properties and also between the former and the transport or non-equilibrium properties [2].

1.2 Properties of molecules

A knowledge of the properties of individual molecule is needed to study the properties of liquids which depend on the collective properties of all the molecules. Quite earlier, it was recognised that molecules must have nearly hard cores and also that they must attract one another. A plot of the potential energy $\phi(r)$ versus distance $r$ for two molecules of nearly spherical shape is as shown in Fig.1.1.

A large energy is required to push the centres of two molecules much closer than OA. This distance is called 'gas-kinetic diameter'. The interaction energy is repulsive at very short distances and weakly attractive at somewhat longer distances. A qualitative explanation of this type of interaction can be given in terms of the quantum mechanical picture of an atom or molecule [2].

1.3 Qualitative Quantum Picture

The molecule is made up of positively charged nuclei each surrounded by an electron cloud. At large distances the mutual
perturbations of the electron clouds of two molecules which do not have permanent dipole moments give rise to London attraction. The corresponding energy is expected to vary as the inverse sixth power of the distance. As the two molecules are pushed closer together, the electrostatic repulsion between the nuclei begin to be important in addition to mutual distortion of the electron clouds around the nuclei. The net result is a repulsion, but this is much harder to calculate numerically than to calculate the attraction, and is sometimes represented as a power law [2].

1.4 Need of molecular nature for liquid state properties

As long as a liquid was thought of as having a continuous structure, we could accept its physical properties without trying to explain them [2]. However, the macroscopic properties of liquids are mainly related to the properties of the molecules themselves, their dynamic behaviour and to their arrangement in the liquid state. Even if a number of people are engaged in this area, the main problem of interrelation of macroscopic and microscopic properties remain more-or-less unsolved. Therefore, it is useful to gather information about liquid structures. There are many ways of gathering qualitative information about the structures.

In the quantitative theoretical interpretation and hence prediction of liquid state properties at the molecular level, there are two problems. The first problem arises from our inability to evaluate the collective wave mechanics of many elementary particles and thus to determine the intermolecular and intramolecular potential energy surfaces which govern the motion of molecules in condensed phases, and upon which the macroscopic behaviour of a liquid ultimately depends. The second problem of calculating the thermodynamic and transport properties from the intermolecular potentials represents the hitherto largely unattained objective of liquid state theorists [3].

1.5 How to link the molecular properties with bulk properties

When we introduce a molecular hypothesis, the data we require for the evaluation of bulk properties is merely a prescribed set of intra-
and inter-molecular potentials, and the atomic masses. Then it is necessary to appeal to statistical mechanics for tractable expressions relating these molecular data to bulk properties. Only limited progress with approximate analytical theory of the liquid state has been made since the pioneering work of van der Waals more than a century ago. Major advances have been accomplished with the aid of essentially exact numerical techniques through the advent of modern computers during the past two decades [3].

1.6 Disordered structure and liquid properties

The kinetic theory of liquid is one of a number of fundamental advances. It had long been realised that a liquid is unable to resist shearing stresses permanently because of its disordered structure. It would be expected that a solid, with nearly perfect lattice structure, would resist shear. This is because such a configuration is likely to be one in which the potential energy of a typical molecule is nearly a minimum value. If we have a periodic lattice structure with only occasional imperfections, neighbouring rows of molecules would be changed in relative position by shear, and this can be shown to require work if the interaction between molecules is like that shown in Fig.1.1. If, as in a liquid, there is no lattice structure, then a great many molecular configurations with very nearly the same potential energy exist which can be occupied in turn, and a shear deformation (which does not alter the density or the mean distance between the molecules) can take place relatively easily [2].

1.7 Liquids resemble solids

In 1850 Berthelot produced definite experimental evidence that liquids could withstand tensions of at least tens of atmospheres. This may be taken as a final confirmation of the fact that the forces between molecules are attractive at large distances. In other words, a liquid resists changes of density (that is of mean distance between the molecules) even though it can not resist changes of shape. Berthelot also found that the extensibility of a liquid was numerically about equal to its compressibility. In this respect a liquid resembles a solid and is in
sharp contrast with a gas which expands to fill any space, however large, to which it has access [2].

1.8 Liquids resemble gases

There are many evidences to show that the fluid states, gas and liquid, possess many structural similarities and that both are quite distinct from the crystalline solid state of the same substance. Some of these evidences have resulted from the computer simulations of assemblies of particles that interact with particularly simple intermolecular potentials. But most of them are a consequence of the direct experimental investigation into the structure of liquids and highly compressed gases using X-ray and neutron diffraction.

The diffraction pattern of a liquid is very similar to that of the same substance in the gaseous form when it is above the critical temperature and compressed to a comparable density, and both are totally different to that of the crystalline solid. Diffraction studies on compressed gases have been performed only over the past two decades. Previously, because dilute gases possess no X-ray diffraction patterns apart from those due to internal molecular structure, diffraction studies were used as evidence for the contrary postulate, the similarity of the solid and liquid states. During the same period this misconception was compounded by the application to the liquid state of statistical theories based on the cell model in which the individual molecules are imagined to be confined and to move within cells composed of their nearest neighbours. Such a model is solid-like in nature and imposes too great a degree of structure on the fluid [1].

1.9 Distribution function and integral equation

The concept of the 'distribution function' of a liquid had emerged in the 1920s when X-rays were used to examine liquids. This quantity is the variation of local density that would be measured by an observer at the centre of a typical molecule. No other molecule can approach very much closer than the gas kinetic diameter but at this distance we can surround a rigid sphere by up to twelve others. We can
conclude that a typical molecule is surrounded by 'Chinese boxes' formed by the other molecules in the liquid. This means that as a function of distance from the central molecule, the local density oscillates in the manner shown in Fig.1.2 approaching a constant value at large distances.

Fig.1.2 The distribution function of a typical liquid.

The distribution function is usually denoted by g(r) and it can be determined experimentally by X-ray diffraction or neutron scattering. The value of g(r) is proportional to the number of atom pairs separated by a distance r while the total potential energy of the liquid is proportional to the integral \( \int r^2 \phi(r) g(r) \, dr \), where \( \phi(r) \) is the interaction energy between a pair of molecules with centres at a distance r. Thus if g(r) is known as a function of temperature and density (and if the interaction energy is entirely between pairs of atoms) the internal energy is also known as a function of temperature and density and, therefore, all the equilibrium properties of the liquid can be deduced thermodynamically.

In 1935, Kirkwood showed that the proper mathematical tool for the relationship between g(r) and the interaction function \( \phi(r) \) for a liquid was an 'integral equation'. This equation has never been solved exactly, but Kirkwood and his students were able to solve various approximate versions of it. These amounted to the first apriori calculations of the equation of state of a liquid [2].

1.10 Intermolecular forces and physical properties of matter

All the physical properties of matter depend on the intermolecular forces in them. At low temperatures, the strength and
symmetry of these forces determine the properties of the crystal. In the fluid states at higher temperatures, the symmetry becomes less important [1].

The equilibrium properties of a substance, whether it is solid or fluid, are the result of a balance between the cohesive or potential energy on the one hand, and the kinetic energy of the thermal motions on the other. The translational kinetic energy is the same for all molecules at a given temperature - the classical principle of the equipartition of energy-and it is solely the differences in the strength and types of the intermolecular energies that cause the properties of one substance to differ from those of another at this fixed temperature. If liquids are compared at the same fraction of, say, their critical temperatures, it is found to be different in type and symmetry of the intermolecular energies that are responsible for the differences [1].

1.11 The thermodynamic properties

The equations in this section are applicable to pure substances and to mixtures of fixed composition. Small changes in the energy $E$, the enthalpy $H$, the Helmholtz free energy $A$, and the Gibbs free energy $G$ are given by the following four fundamental equations for systems of constant composition and total mass:

\[
\frac{dE}{TdS} - \frac{PdV}{(1.1)}
\]
\[
\frac{dH}{TdS} + \frac{VdP}{(1.2)}
\]
\[
\frac{dA}{-SdT - PdV} = (1.3)
\]
\[
\frac{dG}{-SdT + VdP} = (1.4)
\]

where $S$ is the entropy. It follows that

\[
\left(\frac{\partial E}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T = -P
\]
\[
\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T = V
\]
\[
\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P = -S
\]
The changes of $E$, $H$, $S$, $A$ and $G$ with temperature are related to the heat capacities at constant volume and at constant pressure:

$$C_v = T \left( \frac{\partial S}{\partial T} \right)_v = \left( \frac{\partial E}{\partial T} \right)_v = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_v \quad (1.8)$$

$$C_p = T \left( \frac{\partial S}{\partial T} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_p \quad (1.9)$$

$$E = A - T \left( \frac{\partial A}{\partial T} \right)_v \quad (1.10)$$

$$H = G - T \left( \frac{\partial G}{\partial T} \right)_p \quad (1.11)$$

The isothermal changes of $E$, $H$, $S$, $A$ and $G$ with volume or pressure can be expressed in terms of $P, V$ and their mutual derivatives. Differentiating Eqs. (1.10) and (1.11):

$$\left( \frac{\partial E}{\partial V} \right)_T = -P + T \left( \frac{\partial P}{\partial T} \right)_v \quad (1.12)$$

$$\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_p \quad (1.13)$$

The pair of Eqs. (1.12) and (1.13) are known as the thermodynamic equations of state.

The three mutual derivatives of $P, V$ and $T$ are named as follows:

$$\left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_P = \alpha \quad (1.14)$$

is the coefficient of the thermal expansion

$$- \left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial P} \right)_T = \beta \quad (1.15)$$

is the isothermal coefficient of bulk compressibility

$$\left( \frac{\partial P}{\partial T} \right)_V = \gamma \quad (1.16)$$

is the thermal pressure coefficient.
The change of \( \rho_p \) with pressure is the compliment of the change of \( \beta_T \) with temperature,

\[
\left( \frac{\partial \rho}{\partial P} \right)_T \left( \frac{\partial \rho}{\partial T} \right)_P = \left( \frac{\partial \rho}{\partial T} \right)_T \left( \frac{\partial \rho}{\partial P} \right)_P
\]

(1.17)

\[
\left( \frac{\partial \rho}{\partial P} \right)_T = \left( \frac{\partial \beta_T}{\partial T} \right)_P
\]

Experimental results are often expressed in terms of these coefficients, and it is therefore useful to rewrite some of the equations above in the following form.

\[
\rho_p = \beta_T \gamma_v
\]

(1.18)

1.12 Mechanical properties

The coefficient of thermal expansion \( \rho_p \), of isothermal compressibility, \( \beta_T \), and of thermal pressure \( \gamma_v \) together with those along the saturation curve, \( \rho_o \) and \( \gamma_o \) may be called the mechanical coefficients of a liquid. \( \beta_s \), \( \gamma_s \) and \( \gamma_m \) are called adiabatic coefficients and \( C_v \), \( C_p \) and \( C_\sigma \) are called thermal coefficients. The most useful distinction is to be found at the molecular level that the mechanical coefficients are determined to a high degree of accuracy, solely by the intermolecular forces, whilst the adiabatic and thermal coefficients depend also on the internal properties of the molecules. Knowing the adiabatic coefficients is of little use without a knowledge of either the thermal or the mechanical coefficients. The measurement of both the adiabatic and the mechanical coefficients is a way of measuring heat capacities without measuring a quantity of heat [1].

1.13 Adiabatic properties

The most important of the adiabatic coefficients is \( \beta_s \), the bulk compressibility. It can be measured directly or can be calculated from the speed of sound. The values of \( \beta_s \) derived from the speed of sound are more common and more accurate. The accurate measurement of this speed is
very inconvenient for sound of audible frequency owing to its long
wavelength and the consequent large size of the apparatus. However,
measurements at ultrasonic frequencies are readily made on samples of
liquid of about 100 cm$^3$ or less. At low frequencies, $U$ is independent of
frequency $f$, and the small coefficient of absorption per unit length, $\alpha$,
increases as $f^2$. This absorption is due to the 'classical' effects of
the shear and bulk viscosity and the thermal conductivity of the fluid.
These values of $U$ are correctly related to the static compressibility,
$\frac{\beta}{s}$, by the equation $\frac{\beta}{s} = \frac{\mu}{s\omega}$. However, many fluids show
dispersion-change of $U$ with $f$ at high frequencies due to relaxation
effects. Therefore the measurements are made at a frequency below the
relaxation region, so as to obtain the static $\frac{\beta}{s}$ [1].

1.14 Liquid mixtures

In this thesis we are mostly concerned about liquid mixtures, and
hence a knowledge of them is of significance. A great amount of
experimental and theoretical work has been done on the properties of
liquid mixtures. They provide one way of studying the physical forces
acting between two molecules of different species. However, they are not
the most direct source of such information. There is difficulties in
interpreting the properties of liquids in terms of the intermolecular
forces. The use of liquid mixtures is now becoming more important to
obtain information regarding the equilibrium and the transport
properties. They are also useful for the study of strong specific forces
between different molecules [1].

1.15 Limitations of the studies using liquid mixtures

There is now less emphasis than hitherto on attempts to explain
the properties of mixtures solely from a knowledge of those of the pure
components. Such attempts rest upon the fallacy that the force $(A-B)$
between two molecules of species $A$ and $B$ is always determinable from
the strengths of the forces $(A-A)$ and $(B-B)$. If it were true that $(A-B)$
forces were always some 'average' of the $(A-A)$ and $(B-B)$ forces, then the
properties of a binary mixture would be predictable, in principle, solely
from a knowledge of those of the two pure components. However, such
averaging is not universally valid. It is true that for very simple substances and for the prediction of relatively crude properties there are suitable averages of the intermolecular forces. However, such averaging is unsatisfactory for many classes of substances and inadequate for the detailed interpretation even of the simplest mixtures. One should rather take the observed properties of a binary mixture as an experimental source of information about the (A-B) forces [1].

1.16 Introduction of extra degrees of freedom

The study of liquid mixtures also provides information about new phenomena which are not present in pure substances. The most interesting of these are new types of phase equilibrium, which arise from the extra degrees of freedom introduced by the possibility of varying the proportions of the components.

1.17 Liquid mixture studies are appropriate for multicomponent system

The possibilities of a priori prediction are greater in a multicomponent system. The energy of an array of, say, three molecules A, B and C is approximately given by the sum of the energies of the three pairs (A-B), (B-C) and (C-A) considered separately. Any small departure of the total energy from this sum can probably be represented adequately by an average of the corresponding departures in the pure components. It should be possible, therefore, to predict the properties of a multicomponent mixture from a knowledge of those of the pure substances and of all the binary mixtures. However, even these predictions can be made only by appealing to our knowledge of the intermolecular forces and so are outside the scope of classical thermodynamics [1].

1.18 Estimation and prediction

"Estimation" and "Prediction" are used as if they were synonymous although the former carries the frank implication that the result may be only approximately correct. Estimates may be based on theory or on correlations of experimental values, or on a combination of both [5].
1.19 Predicting the properties of mixtures

We usually deal with liquid mixtures of two or more components in many cases and would like to know their properties. It would be desirable to be able to estimate or predict easily the properties of mixtures from just the corresponding properties of the components and their concentrations. For accurate prediction of properties of mixtures, other kinds of information in addition to concentration and properties of the components are required. These include interaction between the constituents, particle size and shape, and the nature of the packing found in the mixture. Hundreds of equations (both theoretical and empirical) can be found in the literature for predicting the properties of mixtures. Many of these equations can be shown to be derivable from only a few simple, but very general mixture rule [4].

1.20 Different types of mixtures

Mixtures can be broadly classified into two. (i) Single phase systems in which the components are completely miscible or soluble in each other. (ii) Two-phase or multiphase systems in which the components are insoluble or only partially soluble in each other. In the cases of one phase systems, the interactions between the molecules and how they pack are important in determining the properties of the mixture. In the cases of two-phase systems, the factors which must be considered in the prediction of properties are (i) which phases are continuous and which are dispersed? (ii) What is the shape of the particles, and what is the morphology of the system? (iii) How do the particles pack? (iv) If the particles making up a phase are not spherical, how are they oriented? (v) What kind of interaction occurs at the interphases? [4].

1.21 Properties of interest

The properties of liquid mixtures we are interested in the present studies are

(i) Density of liquid mixtures
(ii) Index of refraction of liquid mixtures
(iii) Sound velocity in liquid mixtures
(iv) Compressibility of liquid mixtures
(v) Other thermodynamic properties
Partial molar quantities

The composition of a mixture may be expressed in several ways, some of which are symmetrical in the components and some of which are not. The symmetrical system is one in which the amount of each component (expressed in moles) is denoted \( n_1, n_2 \) etc, and in which the relative amount of each component is described by its mole fraction \( x_1, x_2 \) etc, where

\[
x_1 = \frac{n_1}{\sum_{i=1}^{\infty} n_i} \quad (i = 1, 2, 3, \ldots)
\]

If \( V \) is the volume of a binary mixture of \( n_1 \) moles of component 1 and \( n_2 \) of component 2, it is interesting to enquire how much of this volume is to be ascribed to the first and how much to the second component. For, in general, \( V \) is not equal to the sum of the volumes occupied by the separate components at the same pressure and temperature before mixing. It is, however, possible in principle to measure the increase in volume \( (\delta V) \) on adding an infinitesimal amount \( (\delta n_1) \) at constant pressure and temperature to a large amount of mixture of known composition. The ratio of \( (\delta V) \) to \( (\delta n_1) \) is the partial molar volume of species 1 in this mixture, here denoted \( v_1 \).

\[
v_1 = \left( \frac{\delta V}{\delta n_1} \right)_{n_2, P, T}
\]

Partial molar quantities are intensive properties which depend only on the pressure, temperature and composition of the mixture. Thus if \( (n_1 + n_2) \) moles of liquid are formed by repeatedly adding small quantities \( (\partial n_1) \) and \( (\partial n_2) \) of the two substances, with the ratio \( (\partial n_1 / \partial n_2) \) a constant, then the total volume is given by

\[
V = n_1 v_1 + n_2 v_2
\]

Thus, \( v_1 \) and \( v_2 \) are functions of the relative composition of the mixture and not of its total amount [1].

1.23 The ideal mixture

The ideal mixture is a hypothetical one whose properties are introduced into the thermodynamic description of real mixtures as
convenient standards of normal behaviour. The term is not restricted to mixtures of two (or more) liquids but may be used, for example, for solutions of both solids and gases in liquids.

1.24 The simplest mixture rules

The rule of mixtures is defined as

\[ P = P_1 \phi_1 + P_2 \phi_2 \]  

(1.22)

where \( P \) is the given property of the mixture, \( P_1 \) and \( P_2 \) are the corresponding properties of the components 1 and 2 of the mixture. The concentration of the components are \( \phi_1 \) and \( \phi_2 \). The concentration terms may be weight fractions, volume fractions or mole fractions depending upon the kind of property being measured. Eq. (1.22) indicates that the property of a mixture is just a linear combination of the properties of the components making up the mixture, and it is a good representation of the experimental facts in some cases. Another simple equation is the 'inverse rule of mixtures' is defined as

\[ \frac{1}{P} = \frac{\phi_1}{P_1} + \frac{\phi_2}{P_2} \]  

(1.23)

This equation is also valid for some mixtures.

Eqs. (1.22) and (1.23) require that one only needs to know the value of the given property for each of the components and their concentrations. It should be noted that the concentrations are not independent of one another but are related by the equation

\[ \phi_1 + \phi_2 = 1 \]  

(1.24)

In many cases, Eq.(1.22) gives the highest value that property \( P \) of a mixture can have while Eq.(1.23) gives the lowest value that \( P \) can have. Thus, Eq.(1.22) is known as the upper bound of a property, and Eq.(1.23) is called the lower bound [4].
1.25 More general mixture rules

In many cases, the simplest mixture rules are not capable of accurately predicting the properties of a binary mixture. If our studies are confined to one phase systems, the general equation is

\[ P = P_1 \phi_1 + P_2 \phi_2 + I \phi_1 \phi_2 \]  \hspace{1cm} (1.25)

where \( I \) is an interaction term which can be either positive or negative. When two substances are soluble in one another, \( I \) is related to such factors as intramolecular interactions or the way in which the molecules pack in the mixture [4].

1.26 Concentration variables

The concentration of the components in a mixture can be expressed in many ways. The correct concentration depends upon the nature of the property of interest and on the kind of mixture. The most common concentration terms used in mixture rules are weight fraction, volume fraction, and mole fraction. In most cases there is no theoretical reason for using weight fraction, but it is often used because of its convenience. Mole fraction usually is the proper concentration term in many cases when the two components are soluble in one another, and when the molecules interact with one another on a number of basis. In some cases the volume of the molecules is more important than their number, then volume fraction is the correct concentration to use. In two phase systems, the components do not intereact with each other on a molecular basis. The volume of the components is the important factor in two-phase systems, so the concentration should usually be expressed in terms of volume fractions. The proper use of a mixture rule requires that the correct concentration variable be used; unfortunately, the proper choice of concentration units is not always obvious.

The weight fraction \( w_1 \) of component 1 is

\[ w_1 = \frac{w_1}{w_1 + w_2} \]  \hspace{1cm} (1.26)

where \( w_1 \) and \( w_2 \) are the weights materials 1 and 2 in the mixture.
\[ \phi_1 = \frac{v_1}{v_1 + v_2} = \frac{\frac{w_1}{\rho_1}}{\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2}} \]  
\[ x_1 = \frac{n_1}{n_1 + n_2} = \frac{\frac{w_1}{m_1}}{\frac{w_1}{m_1} + \frac{w_2}{m_2}} \]

where \( v_1 \) and \( v_2 \) are the volumes, and \( n_1 \) and \( n_2 \) are the number of moles of the components. The densities of the components are \( \rho_1 \) and \( \rho_2 \), and their molecular weights are \( m_1 \) and \( m_2 \). Useful interrelationships are

\[ \frac{1}{\phi_1} = 1 + \frac{w_2}{w_1} \left( \frac{\rho_1}{\rho_2} \right) = \frac{1}{w_1} - \frac{w_2}{w_1} (1 - \frac{\rho_1}{\rho_2}) \]  
\[ \frac{1}{x_1} = 1 + \frac{w_2}{w_1} \left( \frac{m_1}{m_2} \right) = \frac{1}{x_1} - \frac{w_2}{w_1} (\frac{\rho_1}{\rho_2} - \frac{m_1}{m_2}) \]  
\[ \frac{1}{x_1} = \frac{1}{w_1} - \frac{w_2}{w_1} (1 - \frac{m_1}{m_2}) \]

Corresponding equations for \( w_2, \phi_2 \) and \( x_2 \) can be written by switching the subscripts 1 and 2 in the above equations. The concentrations are not related linearly, so the direct substitution of one kind of concentration for another will give a distorted concentration scale in the mixture equation used to predict a property. As a result, the correct value of property \( P \) will not be predicted when the incorrect type of concentration variable is used [4].

1.27 Why mixture rules may be invalid

There are some properties which generally cannot be expected to be predicted by mixture rules. There are other cases in which a mixture equation would be expected to hold, but something unexpected changes as a function of concentration, or some unexpected other phenomenon occurs which makes the equation invalid [4].
1.28 One phase binary mixture

In this thesis we are dealing with one phase mixture. If two (or more) materials are soluble in one another, the system is called one-phase system. Thermodynamically, there is always an entropy of mixing which tends to make two substances miscible in one another. In many cases there also is an energy-of-mixing which can greatly influence the solubility behaviour and thereby many other properties as well. This energy-of-mixing term is the result of some kind of an interaction between the molecules making up the mixture. Interaction effects also may arise from changes in how molecules pack due to preferred orientation. This type of interaction can be largely an entropy effect rather than an energy-of-mixing effect.

For a given composition, the degree of mixing could be very different for different systems. The molecules can be completely random, they can exist in an associated state as clusters, or the two kinds of molecules can exist in various types of complexes. One would expect that the properties of these various kinds of mixtures would be different. These differences in properties would show up as differences in the interaction terms of mixture rules. However, except in a few cases, our theories and experimental techniques are not sophisticated enough to enable us to predict theoretically these interaction terms from the degree or type of mixing that exist in a specific system. Therefore, in most cases, the interaction terms must be determined empirically from experimental data [4].

1.29 The General equation for one-phase mixtures

A useful general equation for predicting properties of one-phase binary mixture is

\[ P = P_1 \phi_1 + P_2 \phi_2 + I \phi_1 \phi_2 \]  \hspace{1cm} (1.32)

where \( \phi \) is the general concentration fraction. The interaction term \( I \) can be either positive or negative, depending upon the system. The new factor
in a mixture which did not exist in the pure components is the interaction between the two different kinds of molecules. Thus, the effect of the interaction term on the given property also depends upon the concentration of each of the two kinds of molecules. Other general mixture equations could be used for one-phase mixtures.

\[ P = P_1 \theta_1^2 + P_2 \theta_2^2 \]  
(1.33)

This equation is identical to

\[ P = P_1 \theta_1 + P_2 \theta_2 - (P_1 + P_2) \theta_1 \theta_2 \]  
(1.34)

Thus, Eqs. (1.33) and (1.34) are the same as Eq.(1.32) for the special case where \( I = -(P_1 + P_2) \).

Gordon and Taylor showed that

\[ K_1 \theta_1 (P-P_1) + K_2 \theta_2 (P-P_2) = 0 \]  
(1.35)

where \( K_1 \) and \( K_2 \) are constants

If \( K_1 = K_2 = K \) then \( P = P_1 \theta_1 + P_2 \theta_2 \) which is Eq.(1.32) when the interaction term is zero.

Eq.(1.33) is a special case of more general equation

\[ P = P_1 \theta_1^m + P_2 \theta_2^m \]  
(1.36)

where \( m \) is a constant. If \( m = +1 \), then Eq.(1.36) gives the usual "rule of mixtures". However, \( m \) can vary between \(-\infty\) and \(+\infty\).[4]

1.30 The graphical method of the mixture equations

The effect of the interaction term \( I \) on the property \( P \) can best be illustrated by graphs made from Eq.(1.32) for specific cases. The value of the property is the same for each of the two pure components in Fig.(1.3). If there is no interaction between the components, that is \( I = 0 \), a horizontal line results in a plot of \( P/P_1 \) versus the concentration \( \theta_2 \).
Fig. 1.3 Plots of Eq. (1.32) with $P_1 = P_2$. Numbers on the curves refer to the values of $I$.

When the interaction is positive, the curves bulge upward so that the value of the property becomes greater than that of the components. This increase in $P$ increases as $I$ increases. When the interaction term is negative, the curves sag below the horizontal line, and $P$ becomes less than either $P_1$ or $P_2$ [4].

1.31 Excess thermodynamic functions

The extent to which real liquid mixtures deviate from ideality is best expressed through the use of thermodynamic excess functions. Most experimentalists express the results of their measurements on the thermodynamic properties of non-ideal mixtures in this form. Such data are used subsequently by a variety of physical scientists. Another principal use of excess functions results from the fact that the statistical mechanical theories of liquid mixtures lead to the prediction of theoretical values of the excess functions. Precise experimental data on carefully selected real mixtures are therefore desirable as test material against which the usefulness of competing theories can be judged [1].

1.32 Index of refraction of liquids

Index of refraction is one of the important properties, similar to density of the liquid. The velocity of a ray of light in a medium is a
constant. In air a ray of light travels with a speed of $2.998 \times 10^8$ m/s, but it travels with a lesser speed in transparent liquids of greater density. As a ray of light passes from air to a liquid, it decreases in velocity. This causes an oblique ray to be bent toward the normal at the point of entry of the ray of light at the surface of the liquid Fig. (1.4).

![Fig. 1.4 A ray of light suffers bending at the surface.](image)

The ratio of the velocity of light in air ($C_o$) to the velocity of light in a liquid ($C_\ell$) is defined as the index of refraction $n$ of the liquid.

$$n = \frac{C_o}{C_\ell} \quad (1.37)$$

Experimentally the ratio of $C_o$ to $C_\ell$ is identical to the ratio of the sine of the angle of incidence in air ($\sin i$) to the sine of the angle of refraction in the liquid ($\sin r$). Therefore, the index of refraction of a liquid is

$$n = \frac{\sin i}{\sin r} \quad (1.38)$$

The calculated index of refraction depends on the temperature of the liquid and the wavelength of the light used. In normal practice, the index of refraction is recorded using the D line of the sodium spectrum ($\lambda = 589$ nm) at the temperature of $20^\circ$C and is denoted by $n_D^{20}$. 

20
As the temperature of a liquid increases, its index of refraction decreases. The decrease in index of refraction per degree Celsius rise in temperature varies slightly from compound to compound, the average value being about $4.5 \times 10^{-4}$. This value may be used to find the index of refraction at any temperature $t$ as

$$n_D^t = n_D^{20} - 4.5 \times 10^{-4} (t - 20)$$

The index of refraction can be determined to an accuracy of approximately one per 10,000 for the pure liquid and is normally recorded using four significant figures. Since the value can be determined with such great accuracy, it is of greater precision than melting points, boiling points and similar physical constants as a means of identification of a pure liquid.

The changes in index of refraction from compound to compound is related to changes in structure. The square of the index of refraction is used to detect hydrogen bond complexes since it is related to hydrogen bonding (6-8).

### 1.33 Molar refraction of liquids

Molar refraction or molar refractivity of a liquid is defined as

$$R_m = \frac{m}{\rho} \left( \frac{n^2 - 1}{n^2 + 2} \right)$$

where $m$ is the molecular weight and $\rho$ is the density of the liquid. The Eq.(1.40) gives the explicit dependence of the refractive index, for light of any one particular colour, on the density, and it should hold good when the density is changed provided that isotropy is preserved. The molar refraction of a substance is the total polarizability of a mole of the substance. From Eq.(1.40) it can be seen that, to a good approximation, the molar refraction of a mixture of two substances is equal to the sum of the contribution due to each substance. Thus if two liquids of molar refractions $R_{m1}$ and $R_{m2}$ are mixed, and if a unit volume
of the first liquid contains \( N_1 \) molecules and of the second \( N_2 \) molecules
then the molar refraction of the mixture will be

\[
R_m = \frac{N_1 R_{m1} + N_2 R_{m2}}{N_1 + N_2}
\]  

(1.41)

In the case of monatomic substances \( R_m \) is called atomic refractivity. If
\( R_{m1} \) and \( R_{m2} \) are the atomic refractivities of constituent atoms of a
compound thus the molar refraction is

\[
R_m = N_1 R_{m1} + N_2 R_{m2}
\]  

(1.42)

The molar refraction has been shown to have both additive and
constitutive properties. As there is a dependence of index of refraction
on structural features, the molar refraction can be of considerable
assistance in the identification of unknown compounds. So molar
refraction have been used to determine the structure of compounds. When a
compound contains two or more double bonds, the value of \( R_m \) depends not
only on their number but also on their relative positions. When the
double bonds are conjugated, the observed molar refraction being higher
than that calculated. This anomaly is known as optical exaltation and it
usually increases with increase in length of conjugation (in unsaturated
chains). Although optical exaltation is characteristic of acyclic
compounds it is also exhibited by cyclic compounds. In single ring
system, benzene, pyridine, pyrrole etc, the optical exaltation is
negligible. This has been attributed to resonance. In polycyclic aromatic
compounds, however, the exaltation may have a large value. In general a
large exaltations are shown by those compounds which exhibits large
electronic effects [9,10].

1.34 Temperature dependence of molar refraction

Molar refraction \( R_m \) is not completely independent of temperature.
Variation is of the order of 1 part in \( 10^4 \) for 1 K difference in
temperature [ie, \( (dR_m/dT) = 10^{-4} \) K\(^{-1}\). In order to avoid the necessity for
temperature corrections, Eikman has on the basis of numerous observation
derived a practical empirical formula which very well satisfies the requirement of temperature independence, \( \frac{n^2 - 1}{n + 0.4} \). This formula has not however acquired general acceptance. Gladstone used a formula \( (n - 1) \frac{m}{P} \).

Theoretically this expression is valid only for gases. However, it has led to the discovery of well marked relationships between molar refraction and constitution. Since Gladstone and Lorentz-Lorentz formulae yield two very nearly proportional series of values for the indices of refraction which lie between 1.35 and 1.5, a region in which the values for very many organic compounds fall [7,11].

1.35 Sound, ultrasound and hypersonic sound

Sound is always a fascination for mankind. Every life begins, encountering the rhythmic low frequency sound produced by the heart beats of its mother. Perhaps the human beings like and love musical sounds because they are exposed to the rhythmic sound from the very early stages of their life. A baby recognizes its mother from her sound. Animals identify their prey and their foe from different sounds. Thus sound has an intimate relationship with life.

Scientifically, sound may be defined as any vibration of a solid, liquid, or gaseous medium in the frequency range of the human ear. Ultrasound is that sound which has frequencies above the upper limit for the human ear, viz. 16 kHz and below about 800 MHz. Sound having frequencies above \( 10^9 \) Hz is called hypersonic sound. The term ultrasonics is used to describe mechanical waves propagated in fluids and solids at frequencies in the range mentioned above. The range of application of ultrasound is becoming steadily greater and the number of scientific and technological workers using ultrasound in one way or another has increased enormously [12]. It has found many uses in medicine, in industry, in laboratory and at home. Doctors use it to image fetuses and to remove kidney stones without resorting to surgery. Industrially, it is crucial for welding plastics, cutting brittle alloys, emulsifying cosmetics and for cleaning equipments. In the laboratory, it is used as a tool to extract information about inter and intramolecular interactions in liquids and to investigate the mechanical and thermodynamic properties.
of solids. In one's house, it can be used for dog whistles, jewelry cleaners and burglar alarms [13,14].

1.36 **Low and high intensity ultrasonic waves**

Small amplitude ultrasonic waves are used in many scientific, technological and medical investigations, while large amplitude ultrasonic waves are used in sonochemistry. High frequency ultrasonic waves can be used in the study of phonon-phonon interactions. High intensity (large amplitude) waves also provide the scientist with a unique way of introducing energy into molecules, quite different from conventional thermal heating and other high energy processes such as using laser light to prey molecules apart. In liquids, the chemical effects of ultrasound result from sound waves interacting with the liquid through a process known as cavitation. Ultrasonic waves can create temperatures as high as those at the surface of the sun, and pressures as high as in the deepest oceans [13,14].

Ultrasonic investigations of solids and fluids have been vigorously pursued during the last seventy years. The velocity of small amplitude waves in a medium is a physical property of the medium connected with density $\rho$ and adiabatic compressibility $\beta_s$. A study of variation of wave velocity under varying conditions provides valuable information about the physical properties and molecular interactions of liquids under such conditions. Successful attempts have been made in recent past to correlate ultrasonic velocity with other physical and thermodynamic properties of liquids in the light of various liquid state theories [15]. Thus ultrasonics has emerged as a powerful tool for the study of various acoustic and thermodynamic parameters in the case of pure organic liquids, binary, ternary and quarternery mixtures of liquids and polymers [16].

1.37 **Ultrasonics and liquid state**

Owing to their simplicity and accuracy, the ultrasonic techniques are most widely applied in the study of liquid state, the most complicated amongst the three states of matter [17]. There is a strict
correlation between the chemical structure, physical structure and molecular grouping of liquids and such parameters as the velocity of sound, the coefficient of absorption of sound and modulus of elasticity. The magnitude and the nature of change in modulus of elasticity and the velocity of sound with the frequency or temperature are determined both by the energy of intramolecular interaction and the energy of intermolecular interaction. A change in the nature of the molecular arrangements, structural changes in the contents and the nature of the components in liquid mixtures and a change in the temperature of a liquid influence the effectiveness of the intermolecular interaction. It is therefore quite obvious that all these factors greatly affect the magnitude and nature of the velocity of sound and compressibility. The latter two quantities thus permit us to obtain two kinds of information, firstly, information on the chemical and physical structure, composition and state of a liquid and secondly, information on the mechanical and thermodynamical properties of liquids [18].

1.38 The search for higher frequencies

The investigation of propagation of sound in fluids was a natural step taken in the course of scientific research. Attention was paid to higher frequencies because they can be dealt with more conveniently than the low ones. In some fluids the increase of attenuation with frequency is not gradual and uniform, instead very definite maxima of attenuation are exhibited, the explanation of which is one of the principal aims of research on ultrasonics [19]. Ultrasonic dispersion—change of velocity with frequency—studies in liquids have revealed the existence of relaxation process of molecular origin. A detailed study of such behaviour at different temperatures and over wide range of frequencies enables one to evaluate the parameters characteristic of the reaction which are not readily obtained by other methods [20].

At low frequencies, $U$ is independent of frequency $f$, and the small coefficient of absorption per unit length, $\alpha$, increases as $f^2$. 


This absorption is due to the classical effects of the shear and bulk viscosity and the thermal conductivity of the fluid. These values of $U$ are correctly related to the static compressibility $\beta_s$, by the equation, $U^2 = \frac{V}{m} \beta_s$ where $V$ is the molar volume and $m$ is the molar mass. The experimental speed is equal to this speed over a wide range of frequencies and amplitudes for most fluids and so may be regarded as an equilibrium property. However, it is sometimes larger than the speed defined by the above equation at very high frequencies where the thermal properties of a fluid depend on the rate of heating. Thus, at high frequencies due to relaxation effects, many fluids show dispersion. $U$ increases slowly with $f$, often over several decades, and contains a non-classical component with a peak at a frequency of $(1/2\pi \tau)$, where $\tau$ is the time of relaxation of the physical process that is responsible for the dispersion. When $f$ is large compared with $\tau^{-1}$, then $U$ assumes a constant but higher value that is not directly related to the static compressibility. These relaxation effects are due to processes of equipartition of energy or change of internal structure in the fluid whose times of relaxation are generally less than $10^{-6}$ s. Such processes have, in the past, been described formally as a bulk viscosity, and this is, indeed, a valid mathematical description of a frequency-dependent coefficient of viscosity is admitted. However, the name is not a helpful one and disguises the nature of the process responsible.

It is usually not difficult to be sure that measurements are made at a frequency below the relaxation region, and so to obtain the static $\beta_s$. One very powerful test has been developed recently by comparing $U$ at a frequency, say, $10^6$ Hz with that of hypersonic waves at frequencies of upwards of $10^{10}$ Hz. If these speeds are the same, then it is unlikely that any relaxation process is occurring. These hypersonic speeds are found indirectly from the Brillouin scattering of light from a laser [1].

1.39 Ultrasonics and investigation of the properties of liquids

Studies with ultrasonic waves have gained importance in recent years. Ultrasonic waves with low amplitude have been used by many scientists to investigate the nature of interactions, which occur between
the molecules of the medium [21], because the properties of ultrasonic radiations have been found to depend on the molecular constitution of the medium [22]. The studies of liquids and liquid mixtures are usually made by measuring ultrasonic velocity and absorption as a function of concentration, temperature and frequency. A departure from linearity in the velocity versus composition behaviour in liquid mixtures has a limited utility. Such a representation does not provide any information about the nature and the relative strengths of the various intermolecular interactions. On the other hand, a number of theoretical and experimental investigation have shown that a representation in terms of the derived parameters (thermodynamic parameters) and their deviations from those given by additive rule, provide a better insight into the intermolecular processes [23]. Therefore attempts have been made to use ultrasonic data in computing the thermodynamic data of liquid mixtures. Thermodynamic data also throw light upon the structure-making and structure-breaking effect of components [24].

1.40 Adiabatic compressibility and its excess value

One of the important thermodynamic parameters which has a direct link with the velocity of ultrasonic waves is the adiabatic compressibility. It has extensive applications in characterising the aspects of physico-chemical behaviour of liquid mixtures such as molecular association, dissociation and complex formation [25]. The works on compressibilities and the excess compressibilities are also useful in understanding the solute-solvent interaction in liquid mixtures and give a better insight into the intermolecular forces [26]. Ravi Meher and Reddy determined ultrasonic velocity in aqueous solutions of alcohols and their densities were measured in glycerol, ethylene-glycol, n-propanol, t-butanol and the data had been used to determine compressibilities using expressions based on Jacobson's theory. The changes in compressibilities with the variations of volume fraction of solute are discussed in the light of the structure breaking and the structure-making properties of the solute in water [27]. Rajendra Naidu and Ramachandra Naidu using ultrasonic methods reported sound velocity and isentropic compressibility of ternary liquid mixtures of methyl ethyl ketone and n-nonane as common
component and one of the homologous series of four 1-alkanols as the non-common component at 303.15 K. They had also determined data for adiabatic compressibilities of binary mixtures of methyl ethyl ketone with n-nonane and n-nonane with one of the alkanols at 303.15 K. The ternary and binary data have been examined in terms of structure breaking and structure-making effects of the common components [28]. Sreenivasalu and Ramachandra Naidu studied isentropic compressibilities and their deviations in binary mixtures of 1,1,1-trichloroethane with 1-alcohols at 303.15 K. They found that the deviations in $\beta_s$ in all the binary mixtures are positive over the whole range of volume fractions. They explained the positive deviations as follows. The hydrogen bonded aggregates of alcohols break up progressively on the addition with 1,1,1-trichloroethane which increases the free spaces between the molecules in the mixtures and consequently a negative deviation in sound speed. This would in turn, give a positive deviation in compressibility [29]. Rajendra Naidu and P.R. Naidu found in the case of binary mixtures of n-octane with 1-alcohols that the deviation in adiabatic compressibilities is positive over the whole range of composition for the systems 1-propanol and 1-butanol with n-octane and both positive and negative deviations are observed in the systems 1-pentanol and 1-hexanol with n-octane. These results were explained as that mixing was accompanied by decrease in intermolecular free space defined by Jacobson in the first two mixtures over the whole range of composition and in the last two mixtures the effects (a) decrease in free space and (b) increase in free space balance each other to different degrees [30].

From the above two papers it is clear that we have to consider yet another thermodynamic parameter known as 'free length' ($L_f$) which has intimate relationship with both sound velocity $U$ and adiabatic compressibility $\beta_s$. On the basis of a model for sound propagation proposed by Eyring and Kincaid, $U$ should increase if $L_f$ decreases as a result of mixing two components. They have indicated that $L_f$ is a predominant factor in determining the variation of $U$ in a solution [31]. The other important functions of interest for the studies of liquid state
are molar volume $V$, van der Waal's parameter $b$, isothermal compressibility $\beta_T$ and viscosity $\gamma$ and their excess values.

Ramamurthy et al found that both adiabatic compressibility and intermolecular free length exhibit negative deviation from ideality over the entire range of composition for the binary mixtures of di-$n$-butylamine with $n$-alcohols. These deviations are attributed to the presence of strong $H$ bond interaction between unlike molecules in the mixtures [32].

Choudary et al used adiabatic compressibility and its deviation from ideal behaviour for binary mixtures of $1,1,2,2$-tetrachloroethane with some ketones and explained the results as due to the existence of weak dipolar interactions between unlike molecules [33].

Vimla Vyas, using ultrasonic method reported the measurement of excess values of molar volume, adiabatic compressibility, free length and available volume of methyl ethyl ketone in solutions of benzene and toluene between 20°C and 60°C and explained the results on the basis of formation of transient complexes. The increase in the negative value of the excess adiabatic compressibility with increase in temperature was explained as that the structure stabilization decreases as temperature increases [34].

Subba Rao and Gopalakrishnan had shown in the case of methanol, $n$-propanol, $n$-butanol and isobutanol with an inert solvent carbon tetrachloride that there is a decrease of velocity and an increase of free length to a certain concentration with increasing mole fraction of the diluent [35].

Dharmaraju et al obtained the excess volumes and excess adiabatic compressibility for binary mixtures of acetonitrile with alcohols and found that they are positive over the entire range of composition. They explained the deviations on the basis of weak complex formation and predominating dissociation of self associated alcohol [36].
In another paper Dharmaraju et al reported the deviations of adiabatic compressibility of binary mixtures of cyclohexylamine with benzene, toluene, chlorobenzene, bromobenzene and nitrobenzene and explained them in terms of interaction between unlike molecules. For benzene and toluene with cyclohexylamine, $\beta_s^E$ values are positive over the whole composition range. In the system cyclohexylamine + bromobenzene, $\beta_s^E$ values are negative for volume fraction greater than 0.5. For the system cyclohexylamine + nitrobenzene, $\beta_s^E$ values are negative over the entire range of composition which was attributed to predominating complex formation [37].

Ambananthan studied o, m and p-toluic acids in dioxane ultrasonically and found maxima in velocities and minima in adiabatic compressibilities. The decrease in adiabatic compressibility or the increase in velocity were attributed to the formation of hydrogen bonds between p-toluic acid and dioxane molecules. Assuming a spherical cage model, he used a relation between free volume and adiabatic compressibility and argued that a decrease in adiabatic compressibility would mean decrease of the free volume available which in turn may be caused by a closer packing of the molecules inside the shell brought about by the formation of associated complexes due to hydrogen bonding. The non-linear behaviour of Rao's constant Wada's constant and van der Waal's constant confirms the association character of the mixture studied [38].

Venkateswarlu et al determined adiabatic compressibilities and deviations in adiabatic compressibilities for binary mixtures of 1-2 dibromomethane with alcohols and explained the results in terms of specific interaction between the components [39].

Agnihotri and Prakash studied using free volume the binary liquid mixtures of cumene with alcohols. The nature and strength of the molecular interaction between the components of the mixture have been explained in terms of a deviation in excess free volume [40].

Shukla et al studied the molecular interaction in binary mixtures of trichlorobutane with benzene, toluene, p-xylene, chloroform and carbon tetrachloride using intermolecular free length [41].

30
Rambabu et al found that both $B_g$ and $L_f$ exhibit negative deviations from ideality over the entire range of composition for the binary mixtures of $\gamma$-butyrolactone with propan-1-ol, butan-1-ol, hexan-1-ol, propan-2-ol, 2 methyl propan-1-ol and 3 methyl butan-1-ol. The negative deviation was explained in terms of strong H-bond interaction between unlike molecules in the mixtures [42].

Govindappa et al explained the deviations in $B_g$ from ideal behaviour for the binary mixtures of 1-chlorobutane with benzene toluene, bromobenzene and nitrobenzene in terms of weak dipole induced dipole and dipole-dipole interactions between unlike molecules [43].